

# PHOTOVOLTAIC CELLS AND THEIR POSSIBLE USE AS POWER CONVERTERS FOR SOLAR ENERGY

DAN TRIVICH

*Department of Chemistry, Wayne University, Detroit, Michigan*

There are a number of possible methods by which one may convert solar energy into other more useful forms of energy. In the past and currently, man has made most use of chemical energy as an intermediate form, either through the growing in sunlight of food plants and trees for wood or the collection of stored remnants of such material such as coal, oil, and gas. The useful work is obtained by the proper release of the chemical energy as in animal bodies or in steam engines. A particularly large proportion of our work requirements of energy is obtained by further conversion of the energy from the steam engine into electrical energy because of the convenience of distribution. Because of this, the possibility of direct conversion of solar energy into electrical power is a particularly fascinating one. While not practical yet, from a competitive cost standpoint, possible methods for doing this already exist.

Devices which show an electrical response to light are called photoelectric cells. This paper surveys the constitution and properties of certain types of photoelectric cells and considers the potentialities of such cells as possible converters of solar energy.

One might classify photoelectric cells as photoemissive, photoconductive, or photovoltaic. Photoemissive cells, or phototubes as they are sometimes called, contain two electrodes in an evacuated glass envelope. One of the electrodes has a special photosensitive surface which releases electrons when the proper light falls on it. By application of a potential difference between the two electrodes, an electron current passes which continues through the external circuit. In the gas-filled phototube, a variation of the vacuum phototube in which a low gas pressure replaces the vacuum, the photoelectrons ionize the gas, resulting in a larger current. Phototubes have been very extensively developed commercially for control and measurement purposes.

Photoconductive cells consist of a special solid material, such as selenium, lead, or thallous sulfide, placed between two electrodes. Light falling on the solid causes a large decrease in the resistance of the cell so that with a fixed potential difference applied between the electrodes an increased current passes. Such cells are also used for control and measurement purposes to a limited extent, particularly for the infra-red portion of the spectrum where most phototubes do not respond.

Both photoemissive and photoconductive cells require an external source of potential, that is, an external source of energy for driving the electrons through the circuit. In such cells, the light merely controls the electrical response rather than generates it. Hence, these cells are not useful for the conversion of solar energy to electrical energy. However, the photovoltaic cells respond to light by generating an electromotive force between two electrodes, which can be used to force a current through an external circuit. Thus, photovoltaic cells require no external battery, the source of energy being the light itself. Because of this characteristic, photovoltaic cells can, in principle, convert solar energy directly into electrical power.

There are two general types of photovoltaic cells, the "wet" and the "dry" types. The "wet" type was discovered first, but the mechanism is still not well understood. A review of this type of cell was given by Copeland, Black, and Garrett (1942). The cells are less stable than the "dry" type, perhaps inherently so, and have therefore received less attention. This paper is restricted to the "dry" type of cell, so that any further reference to photovoltaic cells will be understood to apply to the "dry" type.

Photovoltaic cells are also known by the names "barrier layer," "sperrschicht," "solid," "rectifying," "blocking layer," "valve," and "rectifying layer." The best known cells of this type are the selenium and the cuprous oxide cells. The early history of such cells is given by Lange (1938).

#### THE PHYSICAL CONSTITUTION OF PHOTOVOLTAIC CELLS

Photovoltaic cells in their most common form, such as those used in photographic exposure meters, consist of discs about two inches in diameter and less than one-eighth inch thick.

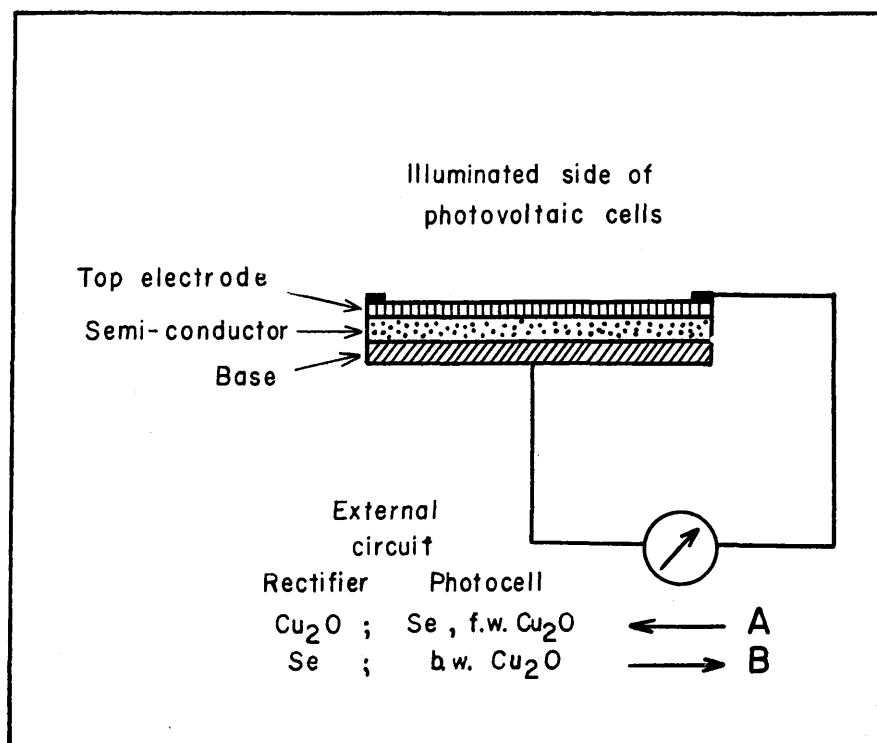


FIGURE 1. Schematic diagram for barrier-layer rectifiers and photovoltaic cells. For photovoltaic cells, the top electrode is either transparent or perforated. A is the direction for easy electron flow for cuprous oxide rectifiers and B, for selenium rectifiers. For photovoltaic cells, the direction of electron flow is A for selenium and front-wall cuprous oxide cells, and B is the direction for back-wall cuprous oxide cells.

Selenium photovoltaic cells are prepared by melting selenium on a sheet of iron, solidifying and recrystallizing the selenium, and applying a top electrode (Preston, 1950). The construction of such a cell may be deduced from the diagram in figure 1. The cell is illuminated through the top electrode, which is, therefore, either perforated or thin enough to be transparent and is often applied by vacuum evaporation or sputtering.

Such a cell will have rectifying properties (Henisch, 1949; Preston, 1950) as well as photovoltaic properties although the details of preparation differ from best attainment of either. In rectification—the conversion of alternating current into direct current—the current passes much more readily from top to bottom within the cell. The conduction is known to be electronic and not ionic, since no electrolysis occurs; and the direction of easy electron flow is from the base into the

selenium to the top electrode. The current passed at any given voltage is proportional to the area of the plate. The resistance in the forward direction drops rapidly in the forward direction with increasing voltage and increases sharply to a maximum in the reverse direction. At a potential of one volt across a typical selenium rectifier cell, the current passing the cell is of the order of several hundred milliamperes per square centimeter in the forward direction and several hundredths of a milliamperes in the reverse direction.

On illumination of a selenium photovoltaic cell, a current passes from the selenium to the top electrode—the electrons flow from the top electrode into the selenium. As shown in figure 1, this is in the high resistance direction and opposite to the direction of easy electron flow for the rectifier. The photocurrent is also proportional to the area of the cell (an important fact in the consideration of energy conversion).

The cuprous oxide photocell, or rectifier, is usually prepared by heating a copper disc to about  $1000^{\circ}\text{C}$ . in the presence of air or oxygen. The surface of the copper is thus converted to cuprous oxide overlaid by cupric oxide. A concentration gradient of oxygen exists in the oxide layers, the concentration on the outside being sufficient to form the cupric oxide, while on the inside only cuprous oxide is formed with a gradient of stoichiometrically excess oxygen. This excess of oxygen is important in determining the conductivity and other properties of the cells. It is common in such cells that the properties are sensitive to traces of impurities, requiring the presence of certain beneficial ones and the absence of certain detrimental ones. The cupric oxide overlay is undesirable merely because of its high resistance and is removed. With a pressed top metal contact, a rectifier is obtained with the direction of easy electron flow being from the copper base into the cuprous oxide as indicated in figure 1. With a perforated top electrode or thin evaporated electrode, a photovoltaic cell is obtained with the direction of electron flow in the high resistance direction, as in the case of the selenium cells; this direction, in the case of the cuprous oxide cell, being from the cuprous oxide into the copper base electrode. Such a cell, called a back-wall cell, is also represented in figure 1.

However, if the top metal electrode is applied by a sputtering technique, a cell of quite different properties is obtained; the principal difference being that the photocurrent now has the electrons flowing from the cuprous oxide toward the top electrode. The cells of this type are called front-wall cells. In addition, these cells produce higher photocurrents and have different spectral sensitivity curves, as compared with the back-wall cells.

According to the theories of Schottky (1942) and of Mott (1948) and others, the physical assemblies described owe their rectifying and photovoltaic properties to the existence of a "barrier layer", at or near the contact of one of the electrodes, to the cuprous oxide or selenium. In the case of the back-wall cuprous oxide photocell and rectifier, the barrier layer lies at the interface at which the cuprous oxide joins the base copper electrode. In the selenium cells and the front-wall cuprous oxide photocell, the effective barrier layer lies at the top electrode interface. The barrier layer acts as a high resistance in the reverse direction for the rectifiers. A satisfactory explanation of the barrier layer and the theories of rectification and photovoltaic action requires an examination of some of the modern theories of the solid state, and, in particular, of a special class of solids—the semiconductors.

#### SOLIDS AND SEMICONDUCTORS

An isolated atom can be described as a massive, positively charged nucleus surrounded by a number of negatively charged electrons possessing definite energies and defined by a set of characteristic quantum numbers. The Pauli principle states that no two electrons can be identical in all of their quantum numbers, or,

stated in another way, no two electrons can occupy precisely the same energy state. However, some of the energy states can have the same energy, i.e., they are degenerate. According to the customary notation, sodium is described by an electronic structure  $1s^2 2s^2 2p^6 3s$ . While the electrons do not occupy precise orbits, the energy levels of the electrons in isolated atoms are fairly definitely fixed, as suggested for the  $3s$  and  $3p$  orbits for sodium in the left of figure 2A.

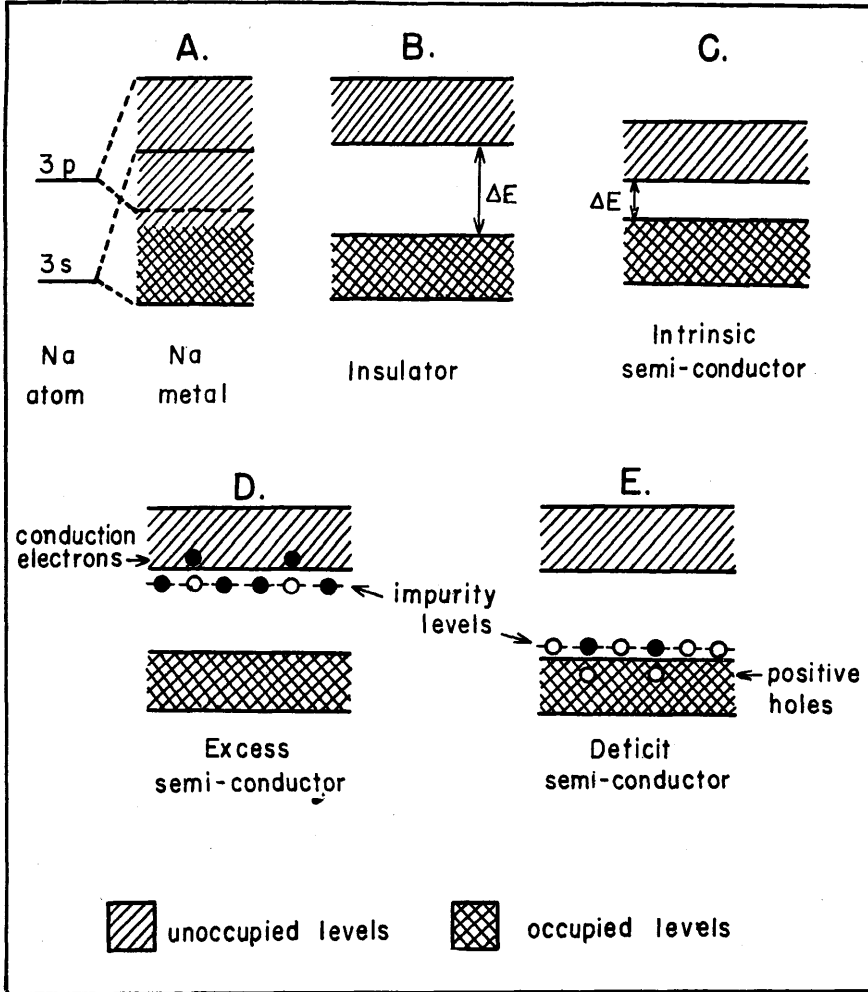


FIGURE 2. Schematic representation of energy levels for electrons in different systems.

When isolated atoms are brought together to form solids, three dimensional arrangements of the atoms result with the outer electrons rearranging themselves into more stable arrangements to contribute the necessary chemical binding. In some cases this requires a transfer of electrons from one type of atom to another creating ions, so that the force of binding arises from the coulombic attraction between the oppositely charged ions. This is true for sodium chloride, cuprous oxide, and many others. In some other types of compounds, the electrons are shared between adjoining atoms, so that the binding arises from highly directional

localized covalent bonds. The arrangements of the atoms in solids depend also on stoichiometrical relationships, relative sizes of the atoms or ions and other factors; and are commonly studied by X-ray diffraction methods. Cuprous oxide has a characteristic ionic structure; selenium can exist in several structures, among them a chain arrangement of atoms held by covalent bonds; and germanium and silicon possess the diamond structure in which each atom is held by four others by covalent bonds in a tetrahedral arrangement.

The energy situation in a solid differs somewhat from that in the isolated atoms. The inner electrons are relatively undisturbed by bringing the atoms together, but the energy levels of the outer electrons are separated and broadened into bands, as shown for sodium in figure 2A. The electrons occupy in general the lowest energies possible, again with the Pauli restriction of no more than one electron per state. At room temperature relatively few electrons are above their lowest possible energies. In the formation of solid sodium chloride, the band arising from 3p levels of chlorine is lower than the 3s band from sodium, and since an additional electron can be accommodated per chlorine atom, electrons are transferred from sodium to chlorine, giving rise to an ionic solid.

The ability of a solid to conduct electric current electronically depends not only on having electrons available, but also on having easily accessible vacancies (energy levels) for them to move into. Good conductors (i.e., metals) result when a band of closely spaced energy levels is only partly filled with electrons, so that nearby unfilled levels are assured, as shown in the energy diagram of figure 2A. Another variation of the metallic structure is obtained when there are enough electrons to fill the band completely, but another band which might have been expected to be empty overlaps the first band.

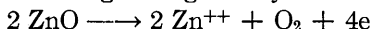
Even when a completely filled band is separated from a completely empty band, there is the possibility of thermal excitation of electrons—the fraction of thermally excited electrons being of the order  $\exp(-\Delta\epsilon/kT)$ . When  $\Delta\epsilon$  is large compared to  $kT$ , the fraction is very small so that an extremely poor conductor (i.e. an insulator) is obtained. This is pictured in figure 2B. If  $\Delta\epsilon$  is not large compared to  $kT$ , an intrinsic semiconductor is obtained, as in figure 2C. The conductivity, which is the reciprocal of the resistivity, depends upon the number of conducting electrons which in turn depends upon the factor  $\exp(-\Delta\epsilon/kT)$ . A usual manner of expressing the experimental data for such systems involves plotting the logarithm of the conductivity or resistivity against the reciprocal of the absolute temperature, since this results in a straight line plot over a considerable range of temperatures.

The electrical properties of semiconductors can be very profoundly altered by the presence of the proper impurities or sometimes by a slight departure from the stoichiometrically correct composition. The reason for this is that the impurities introduce new energy levels near the bands belonging to the semiconductor. Two situations are possible. In one case, as illustrated in figure 2D, the impurity levels containing electrons lie very close to an empty band of the semiconductor. Since the energy gap is small, an appreciable number of electrons is excited into the empty band, which is called a conduction band because the electrons are free to conduct there. The resulting semiconductor is said to be an excess semiconductor or an *n*-type (negative), since its conduction is primarily due to these excess electrons.

In another type of semiconductor, the impurities introduce empty levels near the topmost completely filled band of the semiconductor, as shown in figure 2E. Excitation of electrons from the filled band to the empty impurity levels leaves vacancies or "positive holes" in the previously filled band, so that conduction is now possible in this band. While the conduction is still by means of electrons, another way of viewing the situation is that when a conducting electron jumps into a vacancy, the vacancy moves in the opposite direction. Hence, by this view,

the conduction is effected by means of positive holes moving in the direction of of classical positive electricity. Such semiconductors are known as deficit or *p*-type (positive) semiconductors. Cuprous oxide and selenium are both usually deficit semiconductors.

While in principle, any intrinsic semiconductor can be made into an excess or deficit semiconductor, the usual methods of preparation lead to one or the other preferentially. Cuprous oxide is a deficit semiconductor because the excess of oxygen which exists in the cuprous oxide acts as an electron acceptor, thus creating the positive holes. On the other hand, heating zinc oxide in air tends to drive off some of the oxygen leaving a stoichiometric excess of zinc which serves as an electron donor, thus creating an excess semiconductor. A chemical representation of the situation might be given by:



In the case of the cuprous oxide, the positive hole might be represented by a cupric ion or perhaps an oxygen with a single negative charge. Impurity atoms can occupy either interstitial positions in the crystal lattice or perhaps a regular lattice position with a compensating imperfection elsewhere.

The semiconductors, germanium and silicon, have been extensively studied recently, because of their usefulness in radar detectors and in transistors. Both of these elements have four electrons in their outer orbits as does carbon; and their solid forms assume the diamond structure in which each atom is bound to four other atoms by covalent bonds. Atoms with five outer electrons, such as phosphorus, arsenic, or antimony, can be substituted in occasional lattice positions in place of the germanium or silicon atoms, and since they require only four of their electrons to form the four covalent bonds, the extra electron becomes an excess electron, thus creating an excess semiconductor.

On the other hand, replacement of some of the atoms in germanium or silicon by atoms with three outer electrons, such as boron, aluminum, gallium, or indium, brings about a deficiency of electrons and, therefore, a deficit semiconductor. In some very interesting experiments (Scaff, Theuerer, and Schumacher, 1946), a melt of silicon containing both boron and phosphorus was cooled very slowly, with the result that the first part of the silicon ingot to solidify contained more boron impurity, while the inside contained more phosphorus with a transition from one to the other in between. The result was that the first part was a *p*-type or deficit semiconductor and the last part was an *n*-type semiconductor. In between the two regions, there was a fairly small region where the two effects cancel each other resulting in a high resistance. Such *p-n* junctions are equivalent to the barrier layers and have rectifying and photovoltaic properties.

These ideas of semiconductors and solids, in general, have been very useful in the understanding and development of such diverse things as: radar detectors, transistors, alternating current rectifiers, thermistors, photocells, phosphors, metal oxidation theories, etc.

#### THE METAL TO SEMICONDUCTOR CONTACT

In many of the applications of semiconductors, a metal to semiconductor contact is involved. Further, Schottky showed that for rectifiers and photovoltaic cells this contact must also involve a "barrier layer," which in effect acts as a (variable) high resistance layer. This layer may be a "chemical" barrier, consisting of a very pure semiconductor as in cuprous oxide cells; another compound as in selenium cells; a "physical" barrier, such as a layer of varnish; or a "natural" barrier, inherent in metal to semiconductor contacts.

In a metal, the electrons occupy, to a very large extent, the lowest energy levels possible in a manner dictated by the Pauli principle. The top level occupied at a temperature of absolute zero is called the Fermi level. At any other temperature a few of the electrons from the topmost levels are excited thermally, and the dis-

tribution of the electrons follows the Fermi-Dirac statistics. The amount of energy required to remove an electron from the Fermi level into free space is called the work function is represented by  $W_m$  in figure 3A.

In an excess semiconductor, as shown in figure 3A, there are a few electrons in the conduction band, being contributed by the donor atoms in the bulk semiconductor. The work function,  $W_s$ , represents the energy required to lift the electron from the bottom of the conduction band into free space. Even at ordinary

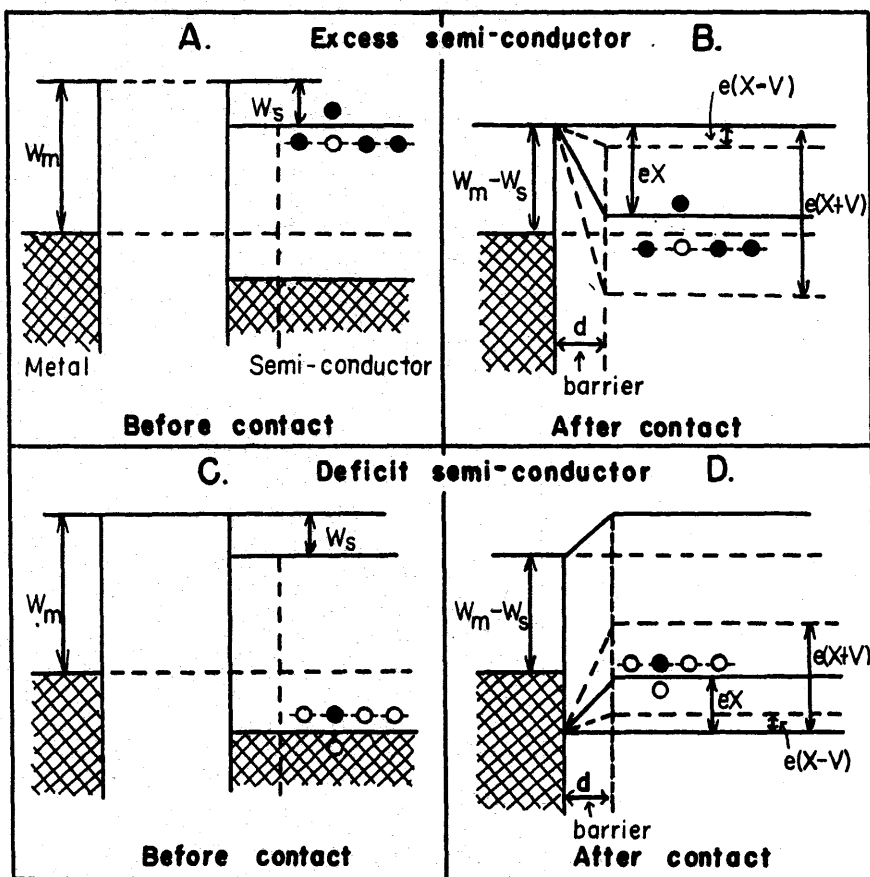


FIGURE 3. The energy level diagrams for metal to semiconductor contacts with chemical barriers at the interface. The changed barrier heights which are due to externally applied voltages and which are responsible for rectification are shown by the indicated dashed lines.

temperatures, a very small number of electrons can acquire the necessary energy to overcome the work function and escape, both in the case of the metal and of the semiconductor.

When the metal is brought in contact with an excess semiconductor, a situation initially like figure 3A results, where the work function for electrons in the metal to escape to the semiconductor is the difference  $W_m - W_s$ . The chemical potential or the number of electrons escaping from the metal is less than from the semiconductor, because of the larger energy requirement, so that there is initially a net electron flow to the metal. This flow results in charging the metal negatively

and the semiconductor positively, thus raising the energy levels of the metal relative to those of the semiconductor. The process continues until equilibrium is attained when the electron flow in one direction is balanced by the flow in the other direction. Equilibrium is reached when the Fermi level of the metal is about midway between donor levels and the bottom of the conduction band of the semiconductor, as shown in figure 3B. The bottom of the conduction band of the semiconductor is depressed by an amount  $X$  on a potential scale, so that the amount of energy required to lift an electron over the barrier is  $eX$ . The barrier, of course, remains as shown, its width being represented by  $d$ .

The case of the contact of a metal to a p-type semiconductor is more involved. In the semiconductor, some of the electrons are bound by the acceptor atoms, so that positive holes exist in the previously filled band, as exemplified by cuprous oxide and selenium. In such deficit semiconductors, the positive holes may be regarded as the conductors instead of electrons, as in the excess semiconductors. The energy level diagrams for a metal and such a semiconductor is shown in figure 3C. In cases of interest, the electrons are initially at lower energy in the semiconductor than in the metal, so that when contact is established between the two, a transfer of electrons from the metal to the semiconductor results. One may regard the transfer of electrons to occur to some of the acceptor atoms in the semiconductor or alternatively regard the electrons as cancelling some of the positive holes in the semiconductor. In any case, the result is that the semiconductor becomes negatively charged with respect to the metal, thus raising the electron levels of the semiconductor relative to the metal to such an extent that the Fermi level in the metal falls about half-way between the filled band and the acceptor levels, as shown in figure 3D. A barrier height of  $eX$  in energy, is created.

#### MECHANISM OF RECTIFICATION

The Mott-Schottky picture described above was devised particularly to explain the mechanism of rectification of electric current, and it succeeds quite well in this. If an excess semiconductor in contact with a metal is made negative, with the respect to the metal, by a voltage  $V$  from an external source, the energy levels of the electrons in the semiconductor are raised by an amount  $eV$ , as shown in figure 3B. The equilibrium is upset, so that a net transfer of electrons from the semiconductor to the metal results. Another way of viewing the situation is that the barrier is reduced to  $X - V$  by the negative voltage on the semiconductor. The direction of easy electron flow is called the forward direction for the rectifier. For the reverse direction when the metal is negative with respect to the semiconductor, the barrier is increased to  $X + V$  thus setting up a high resistance for electron flow.

For the case of the deficit semiconductor in contact with a metal, a negative potential on the semiconductor increases the barrier height to  $X + V$ , as in figure 3D, so that this is the high resistance direction. Making the metal negative decreases the barrier to  $X - V$ , so that the direction of easy electron flow is from the metal to the semiconductor as shown. This is the situation for selenium and cuprous oxide semiconductors.

A more unified point of view of both types of semiconductor rectifiers would be to consider that a negative potential on the excess semiconductor is required to hasten the current carriers (the electrons) toward the metal. For the deficit semiconductor, a positive potential on the semiconductor drives the current carriers (the positive holes) toward the metal.

The discussion here has been limited to chemical barrier layers, but equally satisfactory explanations have been made for other types of barriers. Also, this discussion has treated the barrier as one of constant width and variable height and has implied movement of the conductors over the barrier. Other treatments consider the variation of the width of the barrier, say with applied potential, and



the penetration of the barrier by conductors by tunnelling mechanism. Another phenomenon that should be mentioned here is that the junction between a *p*-type and an *n*-type semiconductor constitutes a barrier with rectifying and photovoltaic properties (Scaff, Theruerer, and Schumacher, 1946). (In transistors, where amplifying properties are desired, such that a small signal at a junction can control a large current across the junction, a further refinement involves a sandwich of a *p*-type semiconductor between two zones of an *n*-type semiconductor, creating a so-called *n-p-n* junction. The double barrier created constitutes a potential "hook" which is sensitive to small potentials applied on the *p*-type slab relative to one of the *n*-type slabs. This controls a large current from the *n* slab to the other *n* slab across the junction).

Another variation of the barrier layer theory is the theory of surface states due to Bardeen (1947). The surface of a semiconductor cannot have exactly the same electronic structure as the bulk of the semiconductor. If new energy levels exist at the surface which are in the forbidden zone of the bulk semiconductor, the surface may act as a metal with respect to the interior. By this view, a rectifying barrier is inherent within the surface of a semiconductor, so that in metal-semiconductor rectifiers, the metal serves as merely a contact instead of creating the natural barrier. This theory successfully explains the previously puzzling fact that the properties of rectifiers are not usually dependent on the work function of the metal used. However, in the interests of simplification, these various ramifications of the barrier layer theory are not being further detailed here.

#### MECHANISM OF THE PHOTOVOLTAIC EFFECT

The photovoltaic effect may be explained as an extension of the rectifier theories and in fact the theories of Schottky and Mott were originally devised for the purpose of explaining both effects.

If one considers a deficit semiconductor, such as cuprous oxide, the establishment of a contact between the semiconductor and a metal approximates initially the condition of figure 3C. Because of the difference in the energy levels of the electrons in the metal and the semiconductor, electrons are preferentially transferred from the metal to the nearest acceptor atoms in the semiconductor, which results in charging the semiconductor negatively with respect to the metal, and conversely the metal positively with respect to the semiconductor. The process continues until the rates of transfer of electrons in both directions are the same. This equilibrium situation is reached when the Fermi level of the metal is about half-way between the filled band and the acceptor levels, as shown in figure 3D. Thus, the equilibrium condition is one in which the semiconductor is negative with respect to the metal.

For the purpose of explaining the photovoltaic effect, the mechanism becomes somewhat clearer if a "natural" barrier layer is postulated, in which the metal is in contact with a semiconductor of the same composition as the bulk of the semiconductor, so that the barrier is inherent in the contact. The character of semiconductor in contact with the metal in the case of selenium or of cuprous oxide is not known with any certainty, but it is still widely held, as in early theory, that chemical barriers are present. A third alternative arises based on Bardeen's theory of surface states, but it is believed by some not to apply to selenium or to cuprous oxide.

Figure 4 sketches the situation of the contact between a metal and a deficit semiconductor, with a natural barrier. As described before, electrons are transferred from the metal to the nearest acceptor atoms in the semiconductor, making the semiconductor negative with respect to the metal. This picture differs from figure 3D in that here a gradient of filled acceptor levels exists in the barrier layer.

When a semiconductor is illuminated, the energy,  $h\nu$ , of the light quanta may be absorbed and used to excite electrons from lower levels to higher levels. For

such frequencies of light that the energy of the quanta is sufficient to lift electrons from the filled band to the acceptor levels, a large improvement in conductance during the illumination is obtained, because of the positive holes created. This improvement is called photoconductance. In the bulk of a semiconductor, light of sufficiently higher frequency or shorter wave length can excite electrons from the filled to the unfilled band of the semiconductor, as shown in figure 4. These electrons fall very quickly to empty acceptor levels and some eventually fall to the (nearly) filled band to cancel some of the positive holes.

In a photovoltaic cell in which the semiconductor is in contact with a metal, the acceptor levels in the semiconductor near the metal are already filled due to the charging process required for the attainment of equilibrium. Here, the photo-excited electrons in the vicinity of the barrier cannot fall into acceptor levels so that their life-time in the excited state is longer than those in the bulk semicon-

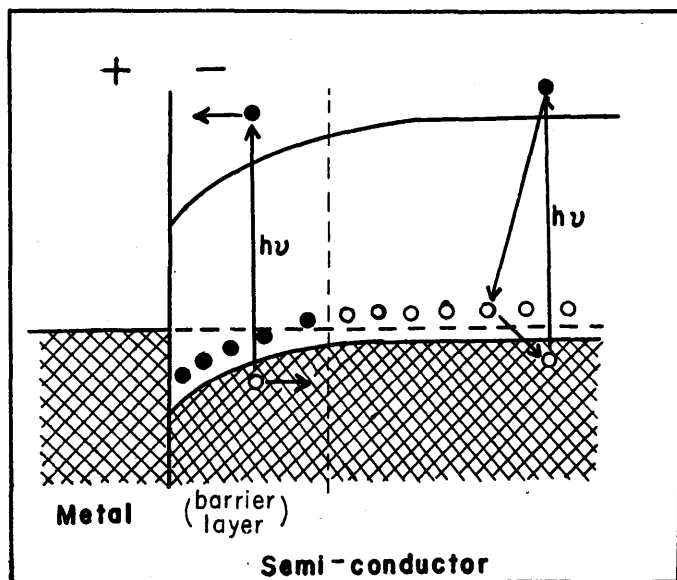


FIGURE 4. The mechanism of the photovoltaic effect. The contact of a metal to a deficit semi-conductor with a natural barrier is shown.

ductor. Because of the space charge which exists at the barrier with the semiconductor negative with respect to the metal, the excited electrons in the conduction band are driven toward the metal. If the circuit is completed externally, the electron current toward the metal is accompanied by a migration of positive holes in the opposite direction, since, of course, the positive holes cannot continue to accumulate in the semiconductor. For an open circuit and high levels of illumination, initially the photoelectrons arriving at the metal will reduce the positive charge on the metal and thus diminish the barrier. This will, in turn, cause a drift of positive holes toward the metal and the steady state, at which the numbers of electrons and positive holes arriving at the metal are equal, will be characterized by a certain open circuit photopotential. The open circuit potential will approach the magnitude of the original barrier, since the net drift of photoelectrons will continue as long as any appreciable amount of the original charging potential remains.

#### PHYSICAL PROPERTIES OF PHOTOVOLTAIC CELLS

The most important property of a photovoltaic cell is its self-generation of current which makes it independent of external sources of potential.

The spectral sensitivity of the cuprous oxide and selenium photocells lies in and near the visible portion of the spectrum, as shown in figure 5. The selenium cell responds from about 3000Å. to above 7000Å. with a maximum response at 5700Å. The front-wall cuprous oxide cell yields a photoelectric current from about 3000Å. to 6000Å. with a maximum at about 5000Å. The back-wall cuprous oxide cell responds from about 6000Å. and continues into the infrared. It is insensitive to wave lengths shorter than 6000Å. because this light is absorbed in the bulk cuprous oxide, so that it does not reach the photosensitive surface. All of the curves represented give relative response for constant light energy with the

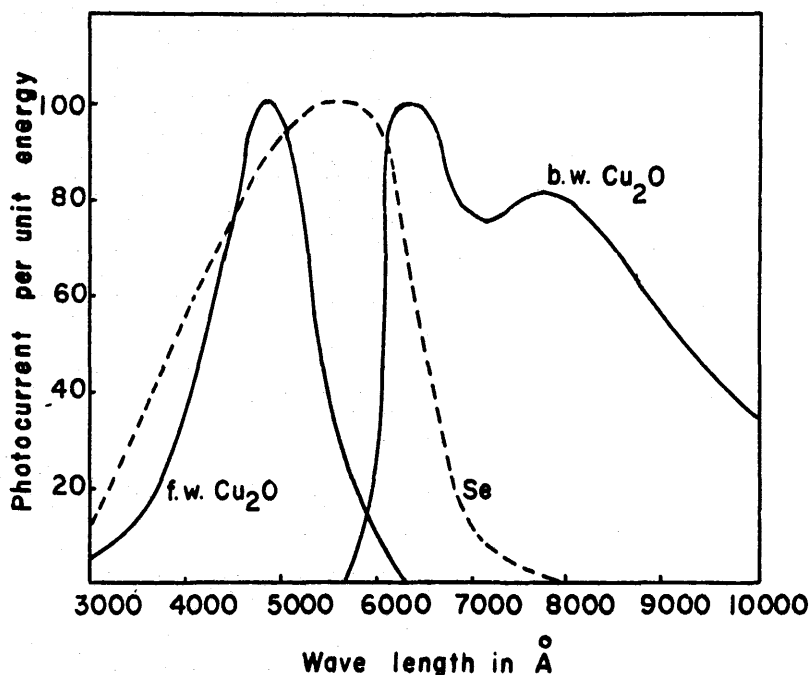


FIGURE 5. The spectral sensitivities of photovoltaic cells of the selenium and front-wall and back-wall cuprous oxide types.

maximum in each case taken arbitrarily as 100. The curves are typical, but the exact values will vary slightly from cell to cell, depending on the manner of preparation and on the light transmission of any substances interposed between the light and the photosensitive surface, such as cover glasses or semitransparent metal films.

The photocurrent depends upon light intensity, but the dependence is affected by other variables. An equivalent circuit is given in figure 6A, where  $I$  is the primary photocurrent,  $C$  is an internal shunting capacitance,  $R_i$  is an internal shunting resistance,  $R_s$  is a series resistance,  $R_c$  is an external contact resistance, and  $R_L$  is an external load resistance. The series resistance,  $R_s$ , is due to the bulk semiconductor, and  $R_c$  is due to the top electrode (the sum of the two being about 50 ohms for a typical 2-inch selenium cell). The internal resistance,  $R_i$ , is due to the barrier and this varies according to conditions, in this case of external resistance and light intensity, as shown by curves  $a$  and  $b$  in figure 6B. Typical values for  $R_i$  are of the order of several hundred to several thousand ohms.

The open circuit potential varies with light intensity approaching a saturation value of about 0.3 volt at high intensities for a typical selenium cell. In addition

to light intensity, the external photocurrent for any given cell depends also upon the external resistance, as is seen by comparing curves  $c^*$  and  $d^*$  in figure 6B. For very low external resistance, the photocurrent varies linearly with light intensity up to quite large levels of illumination. For increasing values of external resistance, the photocurrent departs from linearity at lower and lower levels of illumination. In terms of the equivalent circuit, the photocurrent in the external resistance is given by:  $I_{\text{ext}} = IR_i / (R_i + R_L + R_c + R_s)$ , with the caution, of course, that  $R_i$  is not constant. For measurements with very low external resistances of the order of a few ohms, the slope of linear curve  $c^*$  is about 500 microamperes per lumen for a typical cell of about  $10\text{cm}^2$  area.

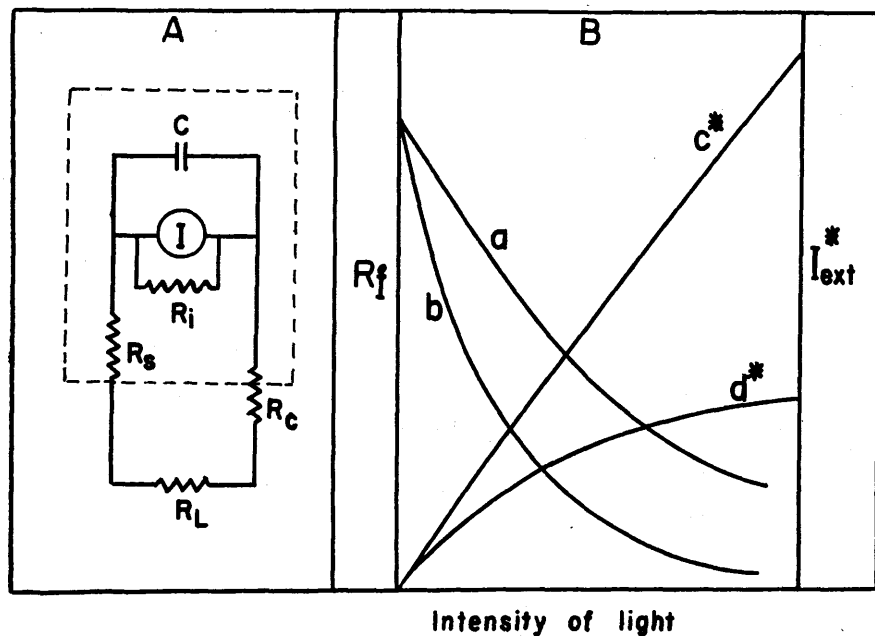


FIGURE 6. A. The equivalent circuit for a photovoltaic cell. The dotted rectangle encloses the circuit elements belonging to the cell proper. B. The dependence of the internal resistance and the photocurrent ( $*$ ) on light intensity. For  $a$  and  $c^*$ , a low external resistance was used, and for  $b$  and  $d^*$ , a high external resistance was used.

The power output is given by the product of the load resistance by the square of the output current (i.e.  $R_L I_{\text{ext}}^2$ ) and this would be a maximum when the external resistance is equal to the internal resistance, if the internal resistance were constant. However, since the internal resistance is not constant, the optimum external resistance varies according to the intensity of illumination.

Temperature also has an effect on current output, but for the present purpose, it is sufficient to state that this variation is in most cases not more than 10 percent for about a  $20^\circ\text{C}$  variation in the vicinity of room temperature. The stability of photovoltaic cells is a chemical and mechanical problem, in that corrosion and such factors determine deterioration. There is no inherent reason for deterioration (electrolysis does not accompany conduction) and, in fact, well-sealed cells have a very long life.

One important factor which arises in the prolonged use of photovoltaic cells is the problem of fatigue. Discounting the external deterioration effects, most of the fatigue appears to be reversible such that the cell recovers after a short rest.

Lange (1938) found that a short-circuited selenium cell exposed to sunlight for 50 days decreased in output by less than 10 percent, with the measurements themselves made under moderate intensities. Measurement of the output under high light intensities shows a relatively quick attainment of a constant output, the time required being of the order of a few minutes.

Another property of photovoltaic cells which is important for certain situations, is that they exhibit an electrical capacitance. However, this is of importance only when the light fluctuations are very rapid, of the order of several thousands per second.

#### CONVERSION OF SOLAR ENERGY INTO ELECTRICAL ENERGY

The consideration of the possibility of conversion of solar energy into electrical energy must begin with a discussion of efficiency. Zworykin and Ramberg (1949) calculate an efficiency of 0.5 percent, using the power output of a selenium cell as 50 microwatts per lumen and the light content of solar radiation as 100 lumens per watt. Direct experimental measurements by Telkes on a cell of 10 cm<sup>2</sup> area receiving illumination of 0.7 watts gave 1.8 milliamperes output at a load voltage of 0.12 volts for an efficiency of 0.03 percent. Preston (1950), with a selenium cell coated with CdO, obtained 0.7 milliamperes per lumen and an open circuit potential of 0.5 volts, which recalling that the load voltage is about half of the open circuit voltage, calculates to an efficiency of over 1 percent. Kosenko and Miselyuk (1948) found silver sulfide cells to be effective from 4000 Å. to 14,000 Å., yielding usually 4 ma. per lumen and sometimes as much as 8 ma. per lumen, with potentials of 0.15 volts. On the other hand, Houstoun (1948) tested several commercial cells, probably selenium, with very much less optimistic results.

There appears to be no obvious theoretical limitation on the efficiency of conversion of solar energy in electrical energy by photovoltaic cells, for example, of the sort that thermodynamics dictates in the case of heat engines. The low efficiencies quoted above represent the present state of development in a field in which no great effort is being made to improve the efficiency of power conversion. In the following calculations an efficiency of 0.5 percent will be used as representing a good present possibility. When a substantial improvement in efficiency is attained, the required photocell area can be reduced proportionately.

Using the average figure for solar radiation, given by Dr. Shaw in this series, of 1000 hp per acre over a 24-hour period, one can calculate a total energy of 3.7 kw-hr per day per square yard. At an efficiency of 0.5 percent, the yield of electrical energy is 0.019 kw-hr per day per square yard. The average domestic consumption of electricity per householder is 5 kw-hr per day, as calculated from data given by Ayres and Scarlott (1952). This means that the average household would require an area of 260 square yards, which would be a plot of 30 ft X 80 ft (roughly the area of a roof on a ranch type home). In winter, where Shaw's figure of 420 hp applies, roughly twice as much area would be needed and in more favorable latitudes and seasons, less area would be required. Of course, since the time of day that electricity is used is not the same as the time when sunlight is available, a storage of energy is implied.

The total consumption of electricity in the United States, for all purposes, is over  $300 \times 10^9$  kw-hr per year or about a billion kw-hr per day and the installed capacity is about 80 million kilowatts, with both rising rapidly. The present capacity could be furnished at the photovoltaic cell efficiency of 0.5 percent by an area of 30,000 square miles, which is a circular area of about 100 miles radius—roughly one-third of the area of any one of the states, Arizona, New Mexico, or Nevada.

The calculations given here are based on present efficiencies. At present, the capital costs of any such installations would probably be prohibitively high compared to present methods of power generation, except for certain isolated

areas or special uses. However, the design of the cells is quite simple and it is easy to envision cheap, large-scale methods for their manufacture, for example, by a continuous strip rolling and coating process. Another minor disadvantage is that current from photovoltaic cells is direct current and the cells are most efficient on a limited load. However, these are not real disadvantages, since motors could be wound for maximum efficiency, and the motors could be used to drive alternating current generators so that the voltage could be stepped up for long line transmission.

Still other problems are details requiring engineering solution. The fatigue at high light intensities could be minimized by using acute angles of incidence for the light. Also, since particular photovoltaic cells have limited spectral sensitivities, a combination of types of cells could be used (e.g., selenium and back-wall cuprous oxide cells complement each other nicely, giving response throughout the visible and a considerable portion of the infrared). Here some sort of non-subtractive light dispersion device would be required. Because of the independent time variation of sunlight intensity, so that production cannot be sensitively tailored to demand, new or re-examined old concepts of electrical energy storage would have to be developed. For example, water could be pumped up-hill during the day and then used to generate power at night, or a chemical product could be made by electrolysis for later use in energy release.

Much of the previous discussion is based on the energy conversion efficiency of 0.5 percent. The obvious starting point for any practical consideration of conversion of solar energy is to improve this efficiency radically. A ten-fold increase of efficiency to 5 percent, a quite reasonable expectation, would mean a ten-fold decrease in the area requirement. As pointed out before, there appears to be no theoretical limit on the efficiency. Past applied research has been concerned more with improvement of stability rather than of efficiency. In view of the large amount of fundamental information clarifying our ideas on semiconductors which has recently been obtained in radar and transistor research, the time is now ripe for research to make substantial advances in the field of photovoltaic cells.

It should be mentioned that another method of converting solar energy into electrical energy is by means of the thermoelectric effect. The principle of the method is as follows: if a junction of two dissimilar materials is maintained at a higher temperature than another similar junction, a potential difference will be set up between the two junctions and a current will flow in a circuit. For solar energy conversion, sunlight would be absorbed, converted to heat, and used to heat the hot junction. A device using this method would be essentially a heat engine and its maximum theoretical efficiency would be limited, as pointed out by Shaw, by the two operating temperatures, as given by thermodynamics. The actual efficiency is a cumulative result of the several parts of the process (efficiency of absorption of light and conversion to heat, reduction in heat losses, etc.) as well as the thermoelectric efficiency itself. The thermoelectric efficiency has been considered by Telkes (1947) and she found experimental efficiencies up to 7 percent with a  $400^{\circ}\text{C}$ . temperature difference, using junctions of lead sulfide with an antimony-zinc alloy. For direct measurements of solar energy conversion, Telkes found about 1 percent efficiency for a flat plate type of generator with a temperature difference of  $50\text{--}70^{\circ}\text{C}$ . and she foresees a probable maximum of 2 percent. With additional light concentration devices, such as mirrors and lenses, to raise the temperature difference to  $300\text{--}400^{\circ}\text{C}$ ., she obtained efficiencies of up to 3.5 percent.

It is difficult to compare the practical potentialities of the various possible methods of using solar energy since in each of them the room for possible improvement is large and the efficiency requirement for feasible operation is fairly small.

The thermoelectric generator, like all heat engines, suffers from the disadvantages of a theoretical limit on efficiency and the necessity of concentrating the light. Its efficiency in conversion of heat into power does not yet compare with vapor heat engines, but this is due probably to the lack of sufficient development. Certainly the thermoelectric effect deserves further investigation as a possible means of solar energy conversion.

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